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METHANE CONTROL DURING SHIPMENTS OF COAL

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METHANE CONTROL DURING SHIPMENTS OF COAL

by

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ABSTRACT

Numerous explosions have occurred in coal mines, storage silos and ship holds as a result of the emission and accumulation of methane released from coal. Recent accidents indicate that control by existing ventilation measures alone may not be sufficient to prevent these accidents from recurring.

This presentation will address the methods being investigated in Canada to eliminate these accidents. It will particularly focus on the results of a research project in which methane oxidizing bacteria are utilized to consume methane as it is desorbed from the coal.

The paper also reviews various factors which influence methane emission from coal and discusses recommended measures necessary to prevent methane explosions during coal shipments.

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CONTRÔLE DU MÉTHANE AU COURS DU TRANSPORT DU CHARBON

par

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RÉSUMÉ

Plusieurs explosions se sont produites dans les mines de charbon, les silos de stockage et les cales de navire en raison des émissions et de l'accumulation de méthane dégagé du charbon. Au cours des derniers accidents, on a indiqué que l'utilisation des systèmes de ventilation comme moyen de contrôle ne suffisent pas à lui seul à prévenir les accidents.

Le présent rapport traitera des méthodes étudiées au Canada dans le but d'éliminer ce genre d'accident. Les résultats d'un projet de recherche dans lequel une bactérie servant à oxyder le méthane est utilisée afin de consommer le méthane à mesure qu'il se désorbe du charbon, seront aussi soulignés.

Le rapport étudie, de plus, divers facteurs qui influencent les émissions de méthane provenant du charbon et discute des mesures essentielles recommandées afin de prévenir les explosions au cours du transport du charbon.

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INTRODUCTION

Explosion of methane during shipment of coal is an ever present hazard. In the recent past methane has caused several serious explosions in ships carrying coal to different parts of the world. In Canada, at least three such explosions have occurred during the last five years in ships transporting coal from the east coast. Effective control of methane is therefore vital both for economic and safety reasons.

An accurate prediction of the likely gas emission pattern during transportation of coal is difficult. Past experience has shown that there are wide variations in methane emission patterns from coals depending on their origin and handling history prior to shipment.

Recent investigations by the Canada Centre for Mineral and Energy Technology (CANMET) have shown that considerable accumulation of methane occurs in coal silos storing washed metallurgical and thermal coals. These investigations have also shown that explosive mixtures of methane and air can occur within the coal pile inspite of forced ventilation of the head space. It is believed that a similar situation exists in coal ship holds. It appears that control by means of head space ventilation alone cannot be considered adequate to prevent methane accumulations in the coal pile void spaces.

In late 1983, a research project sponsored jointly by the Canada Centre for Mineral and Energy Technology, (CANMET), Energy, Mines and Resources Canada and Ship Safety, Canadian Coast Guard, Transport Canada, was initiated with a view to the application of biotechnology to resolve this problem. In general, the method involves oxidizing the methane emitted from coal into non inflammable products using microorganisms.

This paper reviews various factors which influence methane emission from coal and discusses measures adopted in Canada to prevent methane explosion during coal shipment. The progress made to date with regard to biological control of methane and its possible application in coal ship holds is also discussed.

FACTORS INFLUENCING METHANE RELEASE FROM COAL

During the coalification process methane gas is produced as one of the products of decomposition. Most of the gas produced escapes over

geologic time but a considerable amount, in the order of 5 - 20 m^3 of gas per tonne of coal is still retained by the coal mass and is released during mining, storage and transportation of coal.

Laboratory studies have indicated that the surface area of one kilogram of coal can vary between 20,000 m^2 amd 200,000 m^2 depending on the coal type. Methane is present either as free gas or is adsorbed in a thin layer on the coal surface. Adsorption is a surface phenomenon whereby one surface is physically held onto the surface of another. Adsorption processes in general are reversible. Methane exists as a free gas in the pores and fissures and remains at equilibrium with the adsorbed gas; there is a constant interchange of molecules between the free gas and the adsorbed phase.

The volume of methane gas held in coal depends on the volume of gas that can exist as a free gas and also on the coal's gas adsorption capacity. It has also been observed that adsorption capacity of coal increases with the coal rank. Adsorption of methane increases with increase in pressure. Figure 1 shows typical variations in the methane adsorption capacity related to coal rank [1]. Like any other adsorption process methane adsorption capacity is also temperature dependent and decreases with increase in temperature. Accordingly, desorption of methane gas in coal will increase with the increase in temperature. Figure 2 shows the variations in the methane adsorption capacity with changes in temperature [1]. Increase in moisture content also reduces the methane adsorption capacity of coal.

The phenomenon of methane release from coal is rather complex. Laboratory studies including microscopic examination have shown that coal is a very porous and highly microfractured substance. Between microfissures the coal mass is usually homogenous but it contains numerous pores and capillary passages which are connected to the microfissures. The number of microcracks varies from coal to coal and their diameters range from a few microns to a few millimetres. The nature and extent of these microfissures not only depend on the rank of coal but also on its past history such as tectonics influence, stress conditions, depth and method of exploitation.

Methane desorption rate reduces gradually with time from the peak rate at the time of mining. With certain high permeability and porosity coals, desorption may virtually stop within a few days whereas with others

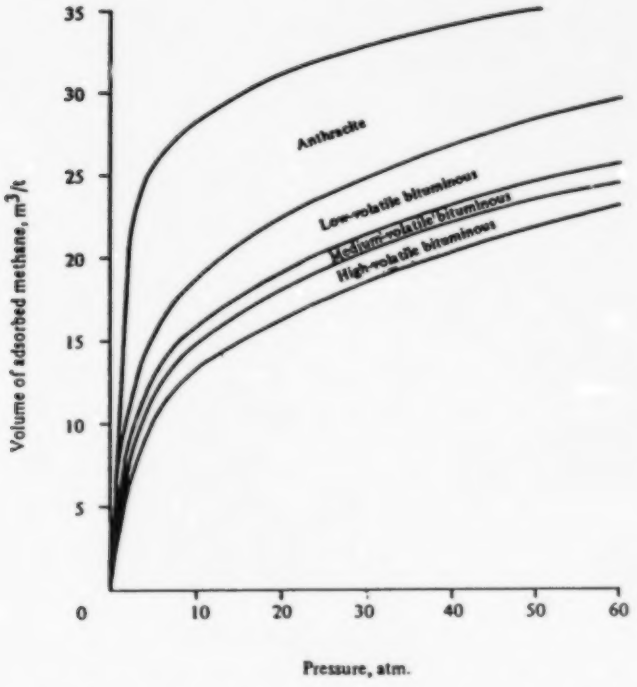

Fig. 1 - Variation of methane adsorption isotherm with coal and rank at 0°C (KIM)

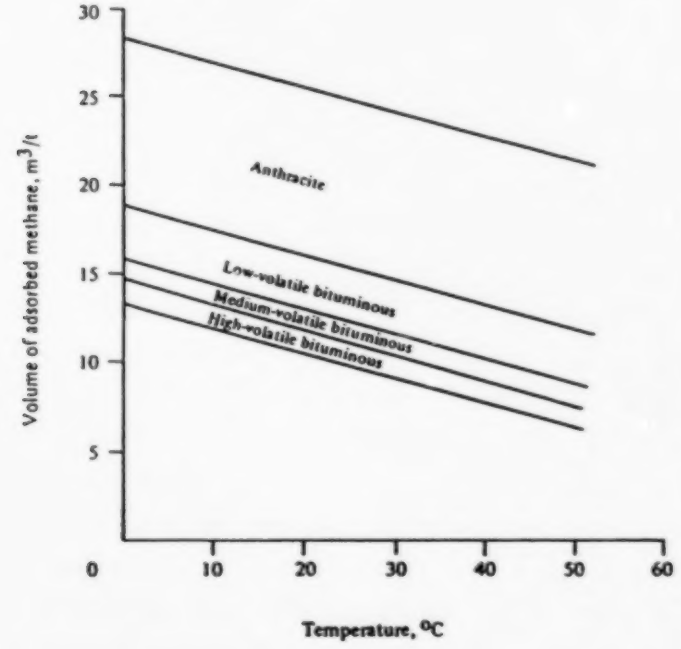

Fig. 2 - Variation of coal adsorption capacity with temperature and rank (KIM).

desorption may continue for months. Degradation during handling can produce more fines and additional fissuration in coal lumps which will increase the methane emission rate.

All these parameters significantly influence the release of methane and result in wide variations in the gas emission patterns during handling and transportation of coal. Because of this, physical measurement of methane release from coal over an extended period is the preferred method of methane desorption measurement.

METHANE DESORPTION TESTS:

Presently there are a number of methods available for carrying out methane desorption tests. A comprehensive review describing the test procedures is available in a recent publication by International Energy Agency [2]. Most of these tests were developed for predicting the emission of methane from coal during mining operations. A careful evaluation of these tests is necessary if an appropriate desorption test procedure is to be developed for use during shipment of coal.

METHANE ACCUMULATION WITHIN COAL SILOS

CANMET has carried out extensive studies [3] on the accumulation of methane in coal silos at a number of coal operations in Western Canada. Methane desorption rates for thermal and metallurgical coals before and after processing were determined and methane and oxygen concentrations were measured in the head space and from within the coal pile. In most ventilated silos methane concentrations in the head space and near the coal surface was quite negligible (often in the order of 0.5% or less) whereas within the coal pile methane concentration varied from 5 to 40% as shown in Figure 3. Oxygen and nitrogen analysis suggested that the gases trapped within the coal pile voids were a simple mixture of methane and air.

Figure 4 shows the inflammability triangle (Coward) for a mixture of methane, oxygen and nitrogen [4]. It is obvious from these curves (Figure 3) that the methane concentration reached the explosive range within the voids of the coal pile in a very short time. The silos where the methane concentration in the voids exceeded the upper explosive limit (15%) are potentially explosive since the mixture in the voids can be made explosive through dilution with air. Such dilution can occur during unloading.

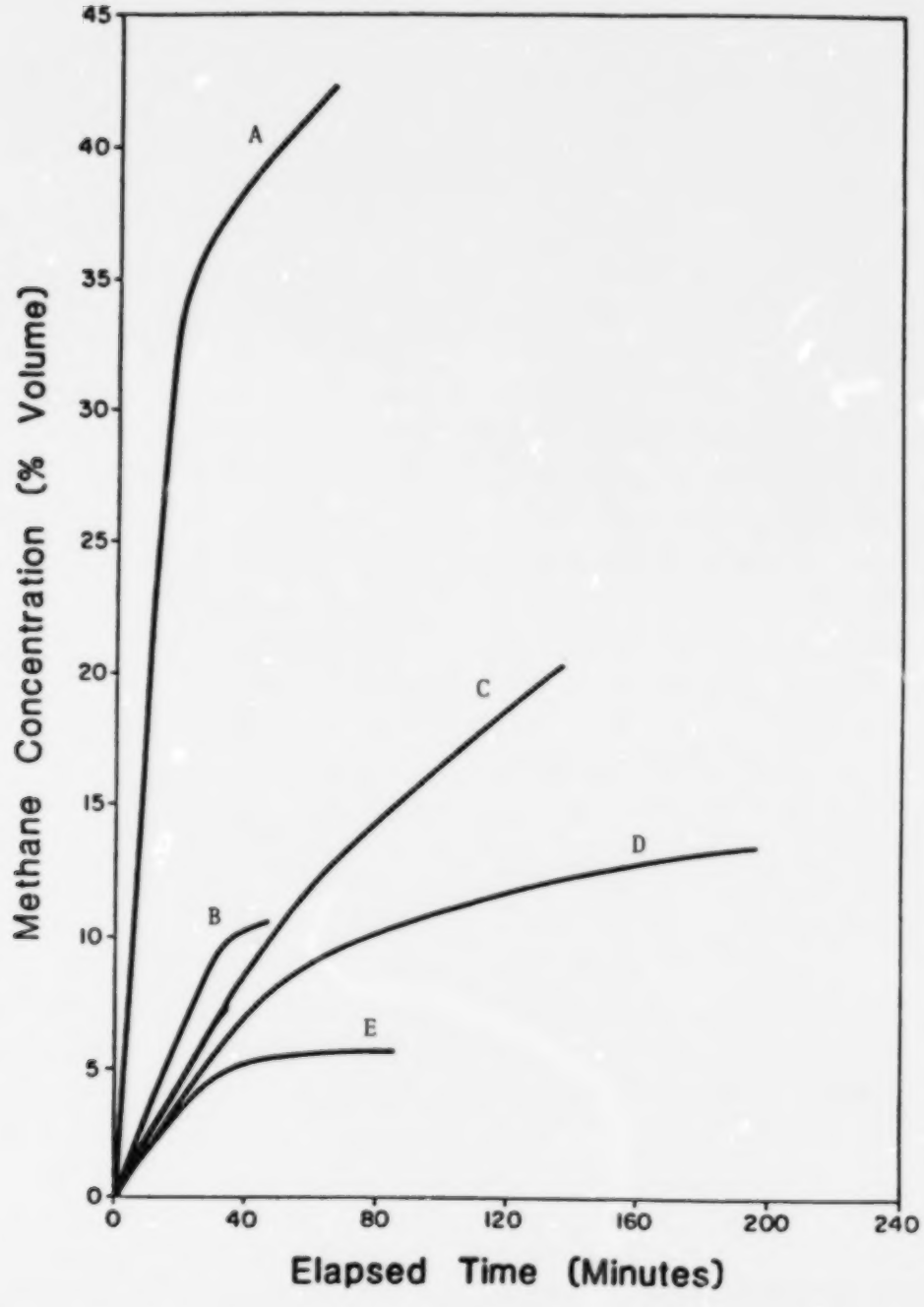

Fig. 3 - Actual Methane accumulation within coal silos for a number of washed coals from Western Canada. Curves ABDE represent washed metallurgical coal and curve C represents washed thermal coal.

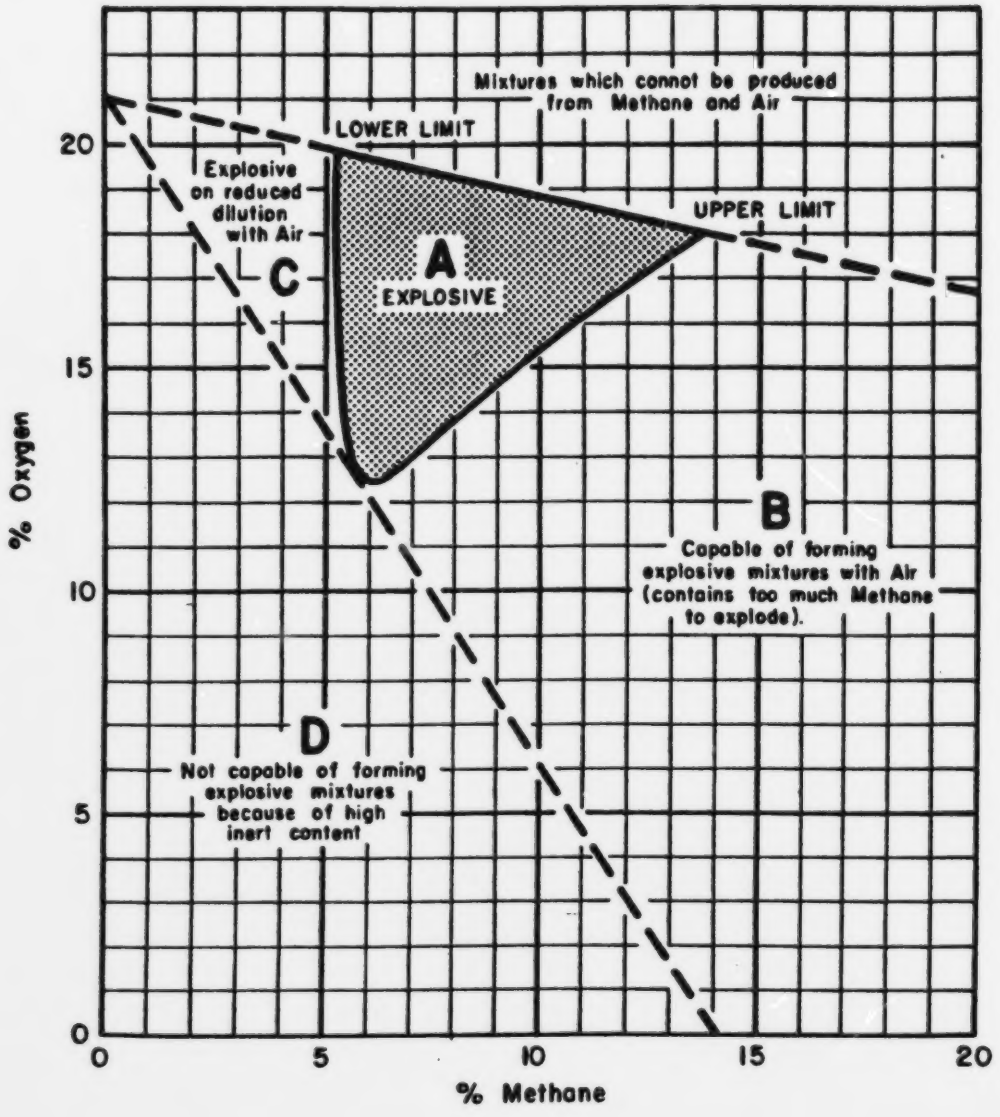

Fig. 4 - Coward's Triangle showing explosibility of methane, oxygen and nitrogen mixture.

PREVENTION OF METHANE EXPLOSION

The first line of defence in the prevention of methane explosion is systematic monitoring of methane.

Because of the potentially explosive nature of methane air mixtures, it is important that methane concentration be measured in all locations in a sea going vessel on a regular basis. Though the explosive limit for methane is between 5 to 15% in air, most regulatory bodies recommend maintenance of the methane percentage below 1.25% for safety reasons. All measuring equipment used should be approved so that the equipment by itself does not constitute an explosion hazard.

A number of direct reading methanometers are commercially available which are capable of measuring a methane concentration of 0 - 5%, often with an accuracy of ± 0.1%. They are battery operated, portable and approved by regulatory bodies for use in an explosive atmosphere. Battery operated personal alarms for the detection of explosive mixtures caused by methane accumulation in hazardous locations are also available.

In the last decade considerable interest has been shown in coal mining operations in the remote sensing and monitoring of methane. Methane sensors are located at strategic points inside the mine and results are telemetered back to a control point where they can be displayed or fed into a computer for analysis or interpretation of data.

Using such systems, unusual emissions or accumulations of methane are readily spotted enabling proper corrective action to be taken immediately. It is suggested that application of such systems to ships transporting coal should be considered.

Methane, being lighter than air, will likely accumulate in the upper regions of cargo spaces. Unless bulkhead and hatch spaces are maintained in a gas tight condition, methane may well find its way into tunnels, peaks, chains lockers, mast houses or other adjacent enclosed spaces. Methane monitoring in these vulnerable areas should be carried out by ship's personnel and the results recorded. In cases of rising concentrations, more frequent readings should be taken so that corrective measures may be implemented without delay.

BIOLOGICAL OXIDATION OF METHANE

In some situations, ventilation of the cargo space alone may not be totally adequate for effective control of methane. In order to deal with such cases, new methods for removal and degradation of methane are being researched. One such method based on biotechnology is being investigated in Canada. This method would involve bringing methane oxidizing microorganisms into contact with the coal to oxidize the methane released to non inflammable products.

Research carried out elsewhere and in Canada [5] indicate that microbiological control of methane is feasible. Bio-oxidation of methane to carbon dioxide follows the pattern shown below:

$$CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCOOH \longrightarrow CO_2$$

The overall reaction may be summarized as:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

For the laboratory tests, methane oxidizing bacteria were isolated from a number of coal samples collected from different Canadian mining operations. Laboratory studies indicate that the rate of methane oxidation to carbon dioxide is quite appreciable using these microorganisms. The methane oxidizing bacteria could oxidize 10 - 12% methane in a 24 hour period as shown in Figures 5 and 6. When added to crushed coal, they could oxidize the methane desorbing from the coal at a sufficiently rapid rate that no methane could be detected in the test flask. Controls which had no added bacteria showed a methane concentration of 6 - 7% within a 48 hour period.

For successful application of this technology during shipment of coal it is essential that the bacterial activity is retained for an extended period of time.

Results of the laboratory studies shown in Figure 7 indicate that almost 60% of the original activity was retained after a period of 100 days when tested with a low sulphur Western Canadian coal.

All methane oxidizing bacteria used in this study are aerobic, that is they require molecular oxygen to oxidize methane to carbon dioxide.

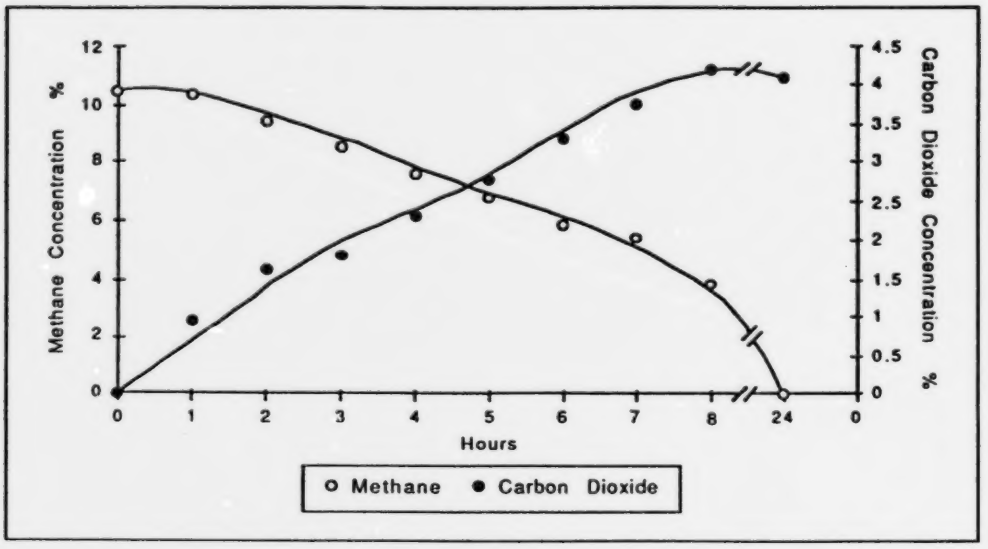

Fig. 5 - Rate of bacterial oxidation of methane in presence of typical Western Canadian coal.

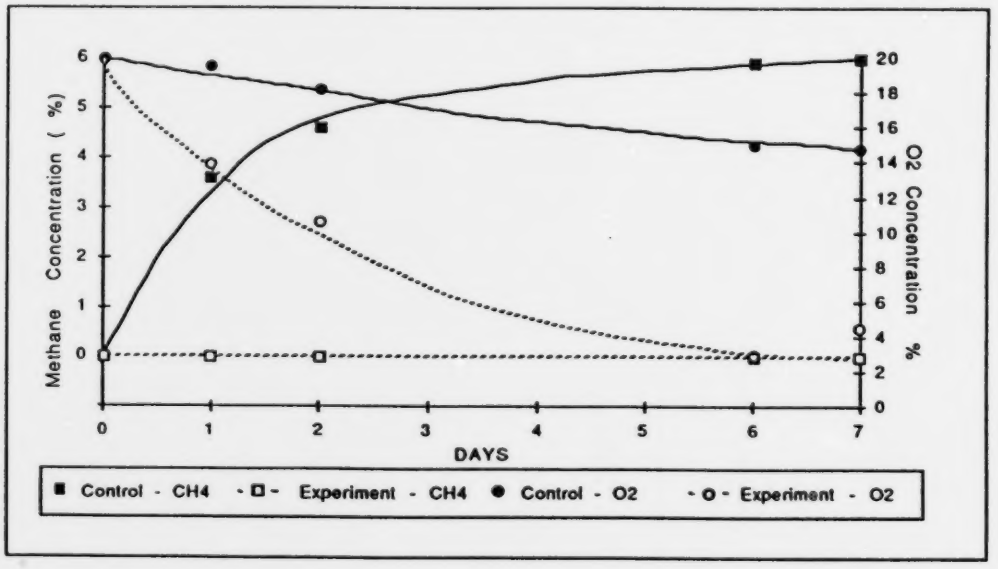

Fig. 6 - Oxidation of methane emitted from pulverized coal with or without addition of methane oxidizing bacteria.

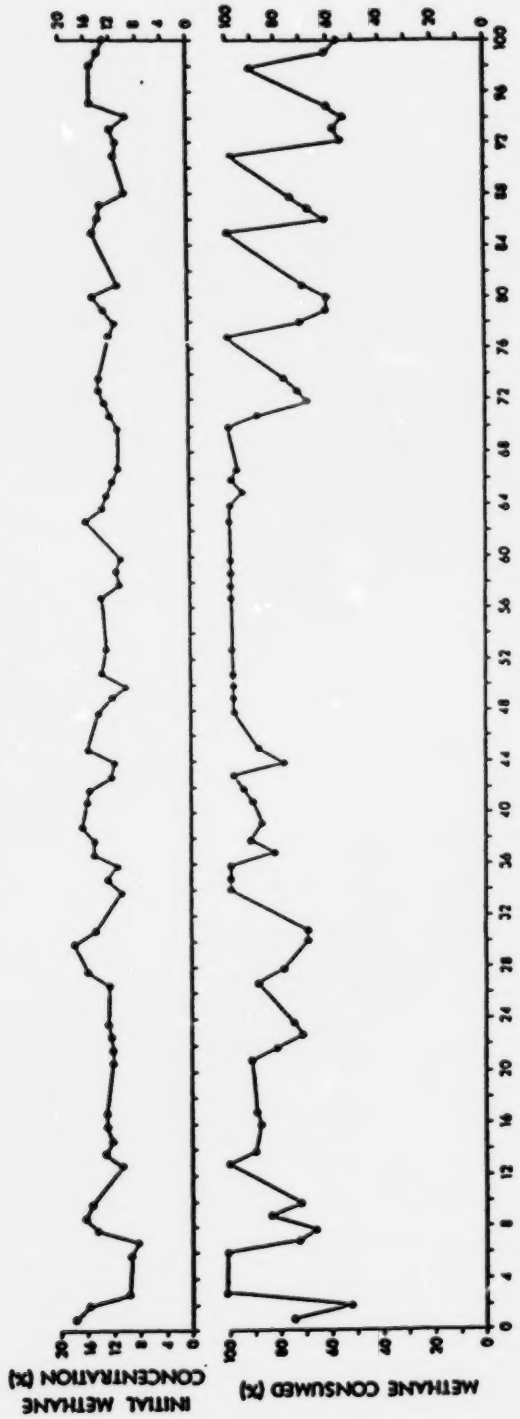

Fig. 7 - Graph showing the activity of methane oxidizing bacteria over an extended period.

Availability of oxygen therefore becomes a controlling factor in determining the amount of methane oxidized when there is a limited supply of oxygen.

Small laboratory scale experiments were successfully scaled up to allow 10 kg of coal to be tested in a model silo and the rates of methane oxidation was found to be quite satisfactory. The results of these experiments (Table 1) show clearly the correlation between the methane oxidized and the oxygen consumed. In all these tests oxygen becomes the controlling factor in determining the total amounts of methane oxidized. All these tests resulted in a non explosive atmosphere within the model silo. These tests further show that there could be a spin off benefit towards prevention of spontaneous combustion during shipment of coal. Lack of oxygen in the coal pile within the ship hold will reduce the possibility of spontaneous heating significantly since spontaneous combustion is an oxidative reaction.

TABLE 1

Correlation between methane oxidation and oxygen consumption for three different coals in a model silo.

Coal	Initial Methane Concentration	Final Methane Concentration	Final Oxygen Concentration
Metallurg-	11.27%	0.67%	3.20%
ical coal	13.04%	3.60%	0.00%
	12.33%	3.40%	1.80%
Thermal	9.20%	0.00%	3.28%
Coal - 1	12.72%	2.30%	0.28%
	13.94%	1.75%	2.50%
Thermal	9.09%	0.00%	4.29%
Coal - 2	15.01%	6.84%	0.00%
	9.53%	0.00%	3.94%

Experiments on a number of coals from Western Canada have indicated that the methane oxidizing microorganisms are quite active with low sulphur coals. However, when high sulphur unwashed coal from Cape Breton in Eastern Canada was tested, the bacterial activity was lost very rapidly. It appears that the oxidation of pyrite present in the coal produced sulphuric acid which lowered the pH of the media to a level where microbial activity was greatly reduced. This was confirmed when Cape Breton coal obtained from the wash plant which removed most of the pyritic sulphur was found not to inhibit the activity of the methane oxidizing bacteria.

Since the presence of pyritic sulphur in the coal inhibits the activity of the methane oxidizing bacteria, three different procedures were tested in the laboratory model to overcome this problem:

- add the bacteria to an inert support which can be placed on top of the coal thus keeping the coal and the bacteria apart;
- remove the pyritic sulphur, and
- adapt the bacteria so that they are more active at low pH.

Preliminary experiments have been completed using all three methods. The best method, if practical and economic, will be to remove the pyrite during coal processing. If this is not possible then suitable inert supports for the microorganisms can be used to remove the methane present in the air space above the coal. However, this will not oxidize methane in the coal pile itself. Manipulation of the organisms themselves has resulted in adapted strains with a broader pH range. However, the lower limit obtainable with this technology is not known at present. Laboratory experiments have reduced the lower limit to pH 5.0 where the bacteria can still remain fairly active.

Experiments are now in progress in which 2 - 3 tons of coal are treated at a time. The sample used for the initial test is a washed coal from Cape Breton, Nova Scotia. The results of this experiment are shown in Figure 8. Two important facts are illustrated by these data. Firstly, there is a decrease in the concentration of methane in the silo after the bacteria are added. Secondly, the amount of oxygen present in the silo is rapidly depleted to insignificant levels. After the bacteria were added the possibility of an explosive mixture within the coal silo was greatly reduced. Thus, this biological technique has the additional benefit of inerting the voids in the coal pile. When the top of the model silo was

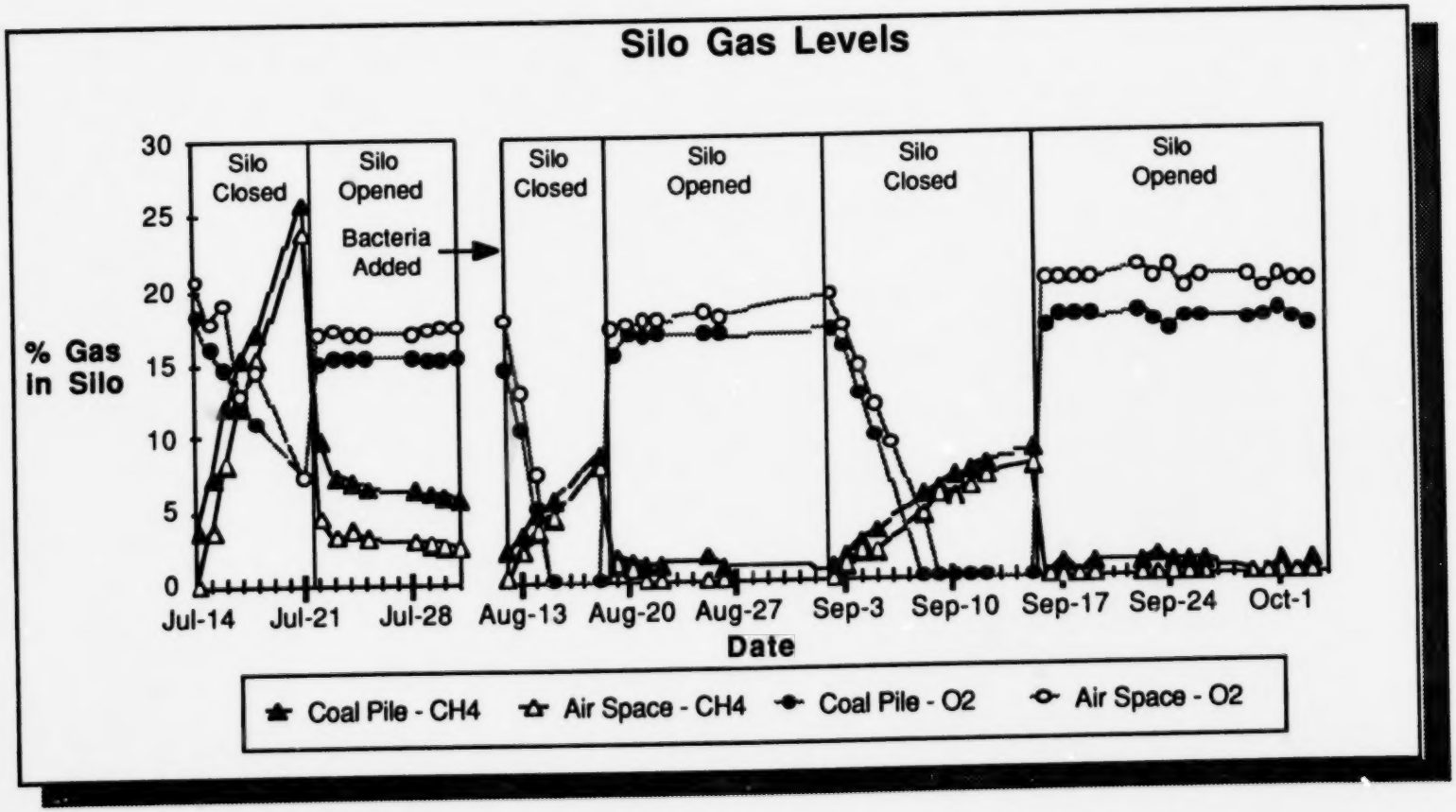

Fig. 8 - Variations in the methane and oxygen concentration in the model silo (2 - 3 tons) before and after spraying the coal with methane oxidizing bacteria.

opened to allov access of fresh air, it was noted that oxygen diffusion took place up to a depth of 1.5 m within the coal pile. It appears that bacterial oxidation of methane can be quite substantial in a ventilated ship hold including the methane accumulated close to the surface of the coal pile.

Further work is nov underway to monitor the effects of controlled ventilation in the airspace above the coal pile since this will more closely mimic the events in an actual ship hold.

An economic assessment was made based on the data presented in this paper in conjunction with other data on the costs of producing the bacteria. These estimates suggest that the cost will vary between $0.50 and $1.00 per tonne to treat 5000 tonnes of coal per day.

INERTIZATION

Explosive accumulations of methane in ship holds could be controlled by using inertization techniques. The principle of inertization is to reduce the concentration of oxygen in the atmosphere. To prevent explosion of a methane air mixture it is necessary to reduce oxygen content to below 12% by volume. The aim is to move the mixture into zone D of Figure 4. Major advances have been made in recent years towards control of coal mine fires through the use of inert gas. A number of heatings in coal mine operations have been successfully controlled using inertization techniques. Inertization makes it safe for self-contained oxygen breathing apparatus equipped rescue people to enter the affected area to fight a fire without fear of an explosion. In most applications to date nitrogen has been used for inerting, however, carbon dioxide and generators which produce oxygen free exhaust gas have also been found effective. The applicability of inertization techniques to prevent explosion and fire in coal ship holds needs consideration.

CONCLUDING RECOMMENDATIONS

(1) All equipment and electrical installations in areas where there is a possibility of gas accumulation must meet the appropriate hazardous classification to eliminate possible ignition of methane.

(2) Effective ventilation of the ship hold cargo head space must be supplemented with special precautions during unloading since potentially explosive methane mixtures can be trapped in the void spaces of the coal pile in spite of the headspace ventilation.

(3) Methane monitoring in all potentially hazardous areas should be carried out by ship personnel on a regular basis. Each ship should be equipped with at least two portable methanometers capable of measuring 0 - 5% (0 - 100% lower explosive limit) of methane gas and at least two officers shall be trained in the use and maintenance of this instrument. All results should be recorded in accordance with instructions given by ship safety officials. [6].

(4) Installation of systems for continuous monitoring of methane should be investigated. Methanometers installed at all strategic locations if interlocked with the electrical system should be able to shut off pover when methane concentration exceeds the statutory limit.

(5) Methane release characteristics for all coals planned for shipping should be studied so that a minimum period of weathering could be established so as to prevent dangerous accumulation of methane. The need for developing an appropriate methane desorption test procedure must be recognized.

(6) Laboratory tests carried out so far indicate that microbiological control of methane is feasible. These organisms can be produced in a bioreactor and sprayed on the coal prior to being loaded into a ship hold. Surface spraying appears to be the simplest method and would certainly be the method of choice during initial large scale tests. Production of microorganisms in a cost effective manner should be investigated. Research and development work needs to be continued with progressively large scale models to establish the effectiveness of this technique.

(7) No single method for methane control will be able to provide complete protection during shipment of coal. Methods based on

biotechnology should not be used as a substitute for good ventilation but as a supplement to provide additional measures for safety.

ACKNOWLEDGEMENT

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